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The Mobile Particles Collision Frequency

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Abstract. The problem of particle collision frequency has been discussed where all particles are mobile. An arbitrary sphere, called sphere of collisions, whose radius is the sum of the radii of the two particles, is considered. The simultaneous sojourn of them in the sphere leads inevitably to collision. New relation for the collision frequency has been derived. The simultaneous collision of two, three and more particles is considered. The new relation provides a much lower value for the collision frequency than the previous one – the great difference is caused by the very low probability for the particles to be found in the sphere of collisions simultaneously. Evaluation of bi-particle and three-particle collisions has been undertaken. At high particle densities the three-particle collisions seem to predominate over the bi-particle ones. These relations concern the rate of the nuclei formation and growth in a homogenous nucleation process.

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1 Introduction

The physics and chemistry of nano sized objects nowadays is very intensively investigated, aiming farther spread in the praxis. The scope of investigations is very spacious – nano rods, nano tubes, fullerenes, graphene. Many kinds of applications based on nano sized materials give promise for the future – gas sensors [1-6], photo detectors [7,8], solar cells [9-11], graphene based THz-transistors [12-14]. Exclusive promising are the perspectives in medicine – antibacterial water filters and viral vaccine [15,16], selective laser nanophotothermolysis of cancer cells targeted by Au nanoparticles [17,18].

Materials, reduced to nano sized scales, reveal totally new features with respect to bulk material. In a nano scale material at the same chemical composition the properties change drastically: band gap increases significantly [19-24]; the solubility increases also [25,26]; inter atomic distance increases [27,28]; melting point decreases very strong – up to several times [29-33]. The nano scale materials demonstrate enhanced mechanical strength due to improved crystal

structure, changes of electrical conductivity and optical property. A transfer of ferromagnetism to super magnetism is observed.

In the nano sized scales the rate of chemical reactions changes drastically. With decreasing particle size the ratio surface/volume increases sharply. For small particles the total number of atoms is almost the same with the number of atoms on the surface. At diameters of 1 nm the ratio of surface atoms to the total number of atoms is $\cong 1$. At larger diameter of about ≈ 10 nm, the ratio is 0,2 [34]. The enormous rate of reactions carried out among nano sized materials might be explained exactly by the high developed surface area. Possible applications of these knowledge leads to intensive investigations nowadays.

The study of the nanoparticles formation and growth is actually for the thin layer deposition of different materials – semiconductors, high temperature superconductors, wave guide materials as well as of bulk crystals growth. These processes obey the same relations beginning with formation of very small nano sized objects called nuclei, their growth and turn into thin layers and bulk crystals.

All the circumstances justify the continuous investigations of nanosized materials – their properties as well as technologies of formation, conservation, application *etc*. The first stage in this series of processes is the collision of atoms, molecules, clusters and the start of interaction among them. The subject of present article is the collision frequency of particles moving continuously. Firstly, the problem of collision frequency of atoms and molecules has been solved in [35,36] with the aim to investigate the rate of chemical reactions. The problem has been solved assuming that a particle is mobile and all others are immobile (frozen). The collisions occur within the volume of the *cylinder of collisions* [37-40]. The number of the collisions per unit time with the frozen molecules yields the collision frequency ν. The particles (atoms and/or molecules) are assumed to be hard spheres and the collisions occur in case when the distance between them becomes less than or equal to the sum of their respective radii. Relation concerning the frequency of collisions, obtained by this approach, almost fully coincides with the given below by eq. 2. The motion of all particles in the medium has been taken into account, assuming that each kind of particles will collide with the same number of frozen particles, divided by two, because at each collision two particles take part.

Another approach concerning the process of nanoparticles formation [41-44] has been developed at the following assumptions: **(1)** particles do not interact with each other and all collisions are accidental; **(2)** particles are spherical; **(3)** they contain one-component atoms with radius r_i, mass m_i and velocity υ_i depending on the number of atoms i in the particle; **(4)** in order to simplify the solution of the problem, it has been assumed that one of the particles is immobile ($\upsilon_k = 0$) and the other one moves by velocity υ_i (Figure 1); **(5)** the medium is isotropic and all directions of movement are equally probable. The probability ω_{ik} for collision of both particles is determined with the aid of the angle of collision α_i

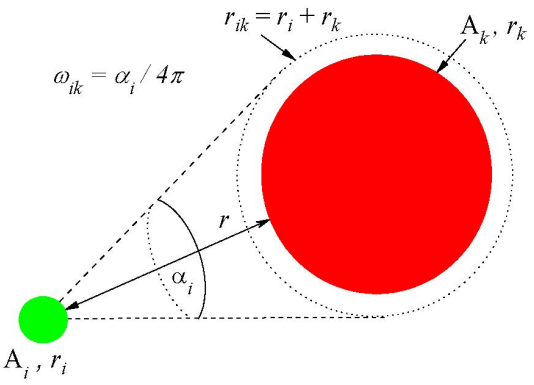

Figure 1. Angle of collision α and the probability for collision ω.

– this is the solid angle, at which the immobile particle A_k is to be observed (generally speaking) from the position of the mobile particle A_i (Figure 1). The ratio of the angle of collisions α_i to the solid angle of the entire sphere 4π, consisting all possible directions of movement, yields the probability for collision ω_{ik}: $\omega_{ik} = \alpha_i/4\pi$. As the particle A_k is immobile, the collision will take place inevitably if the trajectory of the particle A_i lies within the angle of collisions α_i. The number of collisions per unit time obtained by the immobile particle A_k from all the particles a_i follows [41-44]:

$$\nu_{A_k i} = \frac{1}{T_{A_k i}} = \pi n_i \upsilon_i r_{ik}^2 \qquad (\mathrm{s}^{-1}). \tag{1}$$

In the last equation n_i is the density of particles a_i and $T_{A_k i}$ is the period of the collisions. The number of collisions per unit volume per unit time between the particles a_i and a_k is given by

$$\nu_{ik} = \pi n_i n_k \upsilon_i r_{ik}^2 \qquad (\mathrm{cm}^{-3}\mathrm{s}^{-1}). \tag{2}$$

Both approaches assume that one of both particles is mobile and the other is immobile. Under these conditions one supposes a collision of both particles. Both approaches do not take into consideration that at the next moment the particle, assumed to be immobile, in fact, it will not be available at the same place and the collision will not occur.

In present paper using the last approach a new relation for the frequency of collisions of mobile particles has been derived – both particles move by respective velocities υ_i and υ_k. All other assumptions, mentioned above **(1, 2, 3)** and **(5)**, remain the same.

2 Collision Frequency of Mobile Particles

2.1 Simultaneous collisions of two mobile particles

Two arbitrary kinds of particles a_i and a_k are under consideration. Particles move by velocities υ_i, υ_k respectively, have free path lengths L_i, L_k, radii r_i and r_k. The times for covering of the respective free path lengths are τ_i and τ_k. Two particles A_i and A_k ($A_i \in a_i$ and $A_k \in a_k$) and a sphere O_{ik} – the sphere of collisions, have been considered. The sphere is empty (there are no particles) and it is immobile (Figure 2). The radius of the sphere is $r_{ik} = r_i + r_k$ and if both particles simultaneously sojourn in the sphere, they collide inevitably. The aim is to determine how frequently particles a_i and a_k collide with each other within the *sphere of collisions* O_{ik}. In the case, described above (Figure 1), the immobile particle A_k is placed, in fact, just within the sphere of collisions and the collision occurs inevitably if the trajectory of the mobile particle A_i falls into the angle of collisions α_i. This requirement is now not enough – for the collision it is now required both particles to sojourn simultaneously, at the same time, in the sphere.

As the sphere is immobile, eq. 1 is valid with respect to the sphere, providing the number of particles passing through the sphere per unit time. It can be rewritten for each of the particles A_i and A_k. Both equations yield the number of the corresponding particles a_i and a_k, passing through the volume of the sphere per unit time.

$$\nu_{\mathrm{O}i} = \frac{1}{T_{\mathrm{O}i}} = \pi n_i \upsilon_i r_{ik}^2 \quad (\mathrm{s}^{-1}); \qquad \nu_{\mathrm{O}k} = \frac{1}{T_{\mathrm{O}k}} = \pi n_k \upsilon_k r_{ik}^2 \quad (\mathrm{s}^{-1}). \quad (3)$$

$T_{\mathrm{O}i}$ and $T_{\mathrm{O}k}$ are the periods of passing through the sphere of respective particles.

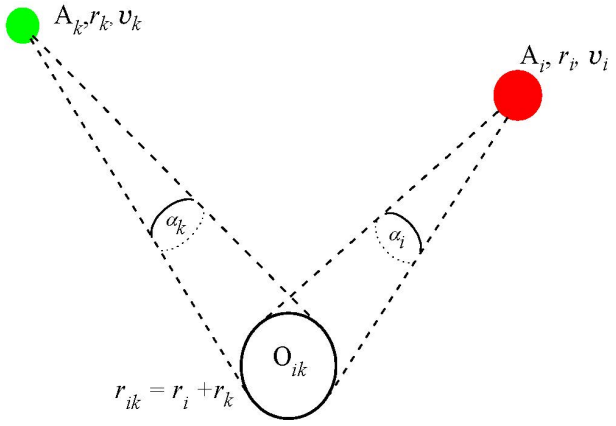

Figure 2. Collision of two mobile particles.

We assume that particles cross the sphere through its centres and the time, spent in the sphere, is $\theta_i = 2r_{ik}/\upsilon_i$ and $\theta_k = 2r_{ik}/\upsilon_k$ respectively. For occurring of a collision between both particles, they must sojourn within the sphere at one and the same time. The total number $\mathrm{N}_{ik}^{\mathrm{O}}$ of particles a_i and a_k passing through the sphere O_{ik} per unit time follows – it is the sum of both eqs. 3.

$$\mathrm{N}_{ik}^{\mathrm{O}} = \pi \left(n_i\upsilon_i + n_k\upsilon_k\right) r_{ik}^2 \quad (\mathrm{s}^{-1}). \tag{4}$$

Some of the particles $\mathrm{N}_{ik}^{\mathrm{O}}$ will pass the sphere without collisions. The rest of them will be liable to collisions. These are those particles a_i and a_k, which fall into the sphere simultaneously. The number of collisions in the sphere per unit time $\overline{\mathrm{N}}_{ik}^{\mathrm{O}}$ will be that part of $\mathrm{N}_{ik}^{\mathrm{O}}$, determined by the probability ψ_{ik}, which provides how frequently particles a_i and a_k are found to sojourn within the sphere simultaneously: $\overline{\mathrm{N}}_{ik}^{\mathrm{O}} = \psi_{ik}\mathrm{N}_{ik}^{\mathrm{O}}$.

As already mentioned θ_i and θ_k provides the time spent in the sphere by the corresponding particle. $T_{\mathrm{O}i}$ and $T_{\mathrm{O}k}$ are the respective time intervals between two consecutive sojourns in the sphere. Then the ratio θ/T is just the probability ψ for a particle to be found to sojourn in the volume of the sphere O_{ik} at an arbitrary time.

$$\psi_i = 2\pi n_i r_{ik}^3 = \frac{3}{2}V_{ik}^{\mathrm{O}}n_i = \frac{3}{2}\aleph_i^{\mathrm{O}}\ ; \quad \psi_k = 2\pi n_k r_{ik}^3 = \frac{3}{2}V_{ik}^{\mathrm{O}}n_k = \frac{3}{2}\aleph_k^{\mathrm{O}}\,. \tag{5}$$

V_{ik}^{O} is the volume of the sphere O_{ik} and the probability ψ is, in fact, proportional to the number $\aleph^{\mathrm{O}}$ of the respective particles belonging to the sphere.

By the calculus of probability [45] the following problem has been solved: let two arbitrary events E_1 and E_2 are taking place separately by the respective probabilities $P(E_1)$ and $P(E_2)$. If both events are independent, the probability for their taking place together is the product of both probabilities for their taking place separately: $P(E_1 \cap E_2) = P(E_1)P(E_2)$ [45].

The events, presented by eq. 5, are independent from each other: the event of sojourn of the particle a_i in the sphere of collisions does not depend on the event for sojourn of particle a_k in the same sphere – we have assumed that the particles do not interact with each other and the collisions are accidental. In this situation the probability ψ_{ik} for the simultaneous taking place of both events at an arbitrary time is the product of the probabilities ψ_i and ψ_k [45]:

$$\psi_{ik} = \psi_i\psi_k = \frac{9}{4}\aleph_i^{\mathrm{O}}\aleph_k^{\mathrm{O}} = 4\pi^2 n_i n_k r_{ik}^6\,. \tag{6}$$

The number of collisions per unit time $\overline{\mathrm{N}}_{ik}^{\mathrm{O}}$ within the sphere O_{ik} between the particles a_i and a_k follows:

$$\overline{\mathrm{N}}_{ik}^{\mathrm{O}} = \psi_{ik}\mathrm{N}_{ik}^{\mathrm{O}} = 4\pi^3 n_i n_k \left(n_i\upsilon_i + n_k\upsilon_k\right) r_{ik}^8 \quad (\mathrm{s}^{-1})\,. \tag{7}$$

To obtain the number of collisions ν_{ik} per unit volume per unit time one must divide eq. 7 by the volume V_{ik}^{O} of the sphere O_{ik}

$$\nu_{ik} = \frac{\overline{\mathrm{N}}_{ik}^{\mathrm{O}}}{V_{ik}^{\mathrm{O}}} = 3\pi^2 n_i n_k \left(n_i \upsilon_i + n_k \upsilon_k\right) r_{ik}^5 \quad (\mathrm{cm}^{-3}\mathrm{s}^{-1}) \,. \tag{8}$$

Each kind of particles (a_i and a_k) is of equal value presented in eq. 8 by the concentration, velocity and size. The entire number of collisions between all particles of the medium per unit volume per unit time one obtains by summing eq. 8 over all values of i and k

$$\nu_{\Sigma} = \sum_{i=1}^{m} \sum_{k=i}^{m} \nu_{ik} = \sum_{i=1}^{m} \sum_{k=i}^{m} 3\pi^2 n_i n_k \left(n_i \upsilon_i + n_k \upsilon_k\right) r_{ik}^5 \quad (\mathrm{cm}^{-3}\mathrm{s}^{-1}) \,. \tag{9}$$

where m is the size of the largest particle a_m, consisting of m-atoms.

2.2 Simultaneous collisions of three mobile particles

In an analogous way one may determine how frequently three mobile particles $A_i \in a_i$, $A_k \in a_k$ and $A_j \in a_j$ will collide simultaneously. The number of particles a_i, a_k and a_j passing per unit time through the sphere is as follows:

$$\mathrm{N}_{ijk}^{\mathrm{O}} = \pi \left(n_i \upsilon_i + n_k \upsilon_k + n_j \upsilon_j\right) \hat{r}_{ijk}^2 \quad (\mathrm{s}^{-1}) \,. \tag{10}$$

Radius $\hat{r}_{ijk}$ is an averaged value over the radii of the different possible spheres of collisions O_{ijk}. The sphere must include the centers of all collided particles. In case of three or more particles, taking part in the collision, there are many kinds of particles arrangements during the collision and three of them are shown in Figure 3 – cases 1, 2 and 3. In case of collision 1 the radius $r_{ijk}^{(1)}$ is maximal, in case of collision 3, $r_{ijk}^{(3)}$ is minimal. Different arrangements provide different values for the radius r_{ijk}; because of that one must use an averaged value $\hat{r}_{ijk}$.

The collision frequency one obtains by multiplication of $\mathrm{N}_{ijk}^{\mathrm{O}}$ by the probability ψ_{ijk} for sojourn of all the three particles at the same time in the sphere of collisions $\hat{\mathrm{O}}_{ijk}$. Because all the events are independent from each other the probability ψ_{ijk} is a product of the probabilities ψ_i, ψ_k and ψ_j

$$\psi_{ijk} = \psi_i \psi_k \psi_j = 8\pi^3 n_i n_k n_j \hat{r}_{ijk}^9 \,. \tag{11}$$

Then for the number of simultaneous collisions ν_{ijk} per unit volume per unit time one obtains

$$\nu_{ijk} = \psi_{ijk} \mathrm{N}_{ijk}^{\mathrm{O}} = 6\pi^3 n_i n_k n_j (n_i \upsilon_i + n_k \upsilon_k + n_j \upsilon_j) \hat{r}_{ijk}^8 \quad (\mathrm{cm}^{-3}\mathrm{s}^{-1}) \,. \tag{12}$$

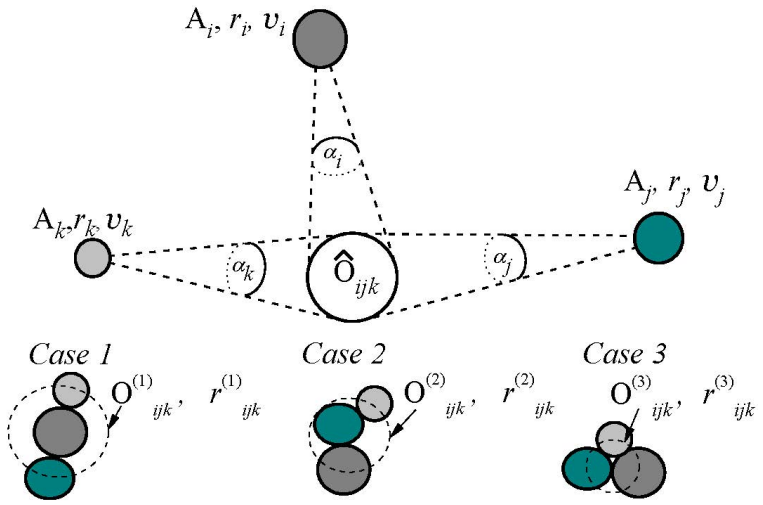

Figure 3. Simultaneous collision of three mobile particles and possible modes of collisions within different spheres O_{ijk}.

By the same way the frequency of simultaneous collisions of an arbitrary number of particles – for example of K-particles, may be derived. The corresponding relations follow:

$$\begin{aligned}
\mathrm{N}^{\mathrm{O}}_{i_1\ldots i_{\mathrm{K}}} &= \pi\left(\sum_{I=1}^{K} n_{i_{\mathrm{I}}}\upsilon_{i_{\mathrm{I}}}\right)\hat{r}^2_{i_1\ldots i_{\mathrm{K}}} \quad (\mathrm{s}^{-1}) \\
\psi_{i_1\ldots i_{\mathrm{K}}} &= \left(2\pi\hat{r}^3_{i_1\ldots i_{\mathrm{K}}}\right)^{\mathrm{K}}\left(\prod_{\mathrm{I}=1}^{\mathrm{K}} n_{i_{\mathrm{I}}}\right) \\
\nu_{i_1\ldots i_{\mathrm{K}}} &= 3.2^{\mathrm{K}-2}\pi^{\mathrm{K}}\left(\sum_{I=1}^{K} n_{i_{\mathrm{I}}}\upsilon_{i_{\mathrm{I}}}\right)\left(\prod_{\mathrm{I}=1}^{\mathrm{K}} n_{i_{\mathrm{I}}}\right)\hat{r}^{3\mathrm{K}-1}_{i_1\ldots i_{\mathrm{K}}} \quad (\mathrm{cm}^{-3}\mathrm{s}^{-1})
\end{aligned} \tag{13}$$

3 Discussion

A comparison of both expressions concerning the frequency of collisions, presented by eqs. 2 and 8, yields the following relation:

$$\chi = \frac{\nu^{eq.8}_{ik}}{\nu^{eq.2}_{ik}} = \frac{9}{4}V^{\mathrm{O}}_{ik}\left(n_i + \frac{\upsilon_k}{\upsilon_i}n_k\right) = \frac{3}{2}\left(\psi_i + \frac{\upsilon_k}{\upsilon_i}\psi_k\right) \ll 1\,, \tag{14}$$

where χ is much smaller than 1. The great difference is to assign to the probabilities ψ_i and ψ_k providing how frequently the particles sojourn in the sphere

of collisions. In eq. 2 it has been assumed that the immobile particle a_k is permanently situated in the sphere of collisions and each mobile particle a_i, whose trajectory lies within the angle of collisions α_i (Figure 1), will collide with them. In this case it is not necessary to investigate how often the particles a_i and a_k sojourn simultaneously in the sphere. Neglecting the motion of particles a_k in case of eq. 2, one cannot take into account how seldom and how long time these particles fall into the sphere of collisions.

Using the classical mechanics (used in many works [46-54]) a rough evaluation of the particles collision frequencies ν_{ik}, ν_{ijk} and probabilities ψ_{ik}, ψ_{ijk} has been undertaken. Particles with sizes r_i, r_k, r_j, velocities υ_i, υ_k, υ_j and densities n_i, n_k, n_j are considered. The frequencies and probabilities have been determined at different values of density. This is in fact the particles behavior in a gas ambient at constant temperature and at different pressure – particle size and velocity remain the same but the density changes.

The particle radius in the case of simple cubic structure has been determined by the expression $r_j \cong 0,62.(j)^{1/3}d_0$ where d_0 is inter atomic distance. Velocity of motion decreases with particle size. We used the relation known from the gas kinetics theory $\upsilon_i = \upsilon_1/\sqrt{i}$ where the single atom velocity is υ_1. Typical values $d_0 \cong 5$ Å and $\upsilon_1 \cong 10^5$ cm/s have been used.

The values of densities, sizes and velocities are nearly equal for particles almost equal in the size (with nearly equal number of atoms). Particles with sizes $i \approx j \approx k$: $i = 500$, $j = 550$ and $k = 600$ have been considered. In case of bi-particle reaction the collision of particles $a_i \equiv a_{500}$ and $a_k \equiv a_{600}$ are under consideration. At densities in the range $n_{600} \approx n_{500} = (10^{10} \div 10^{13})$ cm^{-3} the probability and the frequency of collision vary in the range $\psi_{500,600} \approx 7.10^{-17} \div 7.10^{-11}$ and $\nu^{(8)}_{500,600} \approx 10^4 \div 10^{13}$ cm^{-3}s^{-1} respectively.

At the same time for three-particle reactions among the particles $a_i \equiv a_{500}$, $a_j \equiv a_{550}$, $a_k \equiv a_{600}$, and at low values of densities the probability for collision is negligible $\psi_{500,550,600} \approx 10^{-24}$, and the frequency of collisions becomes negligible too: $\nu_{500,550,600} \approx 10^{-4}$ cm^{-3}s^{-1}. The three-particle collisions will have a poor influence on the particle density, which will be determined by the bi-particle reactions.

At bi-particle collisions the rise of density by one order of magnitude leads to increase of the probability ψ_{ik} by two orders of magnitude and of the frequency ν_{ik} – by three orders. In case of three-particle collisions the rise of density by one order of magnitude leads to increase of the probability for simultaneous collision, ψ_{ijk} by three orders of magnitude and the corresponding frequency ν_{ijk} by four orders of magnitude, illustrated in Figure 4 (see also eqs. 6, 8, 11, 12). One may expect that at densities about 10^{17} cm^{-3} the frequencies of bi-particle and three-particle collisions will become commensurable and both reactions will be in equal value presented in the process of nano particles nucleation. At higher densities one may expect that the frequency of three-particle collisions will pre-

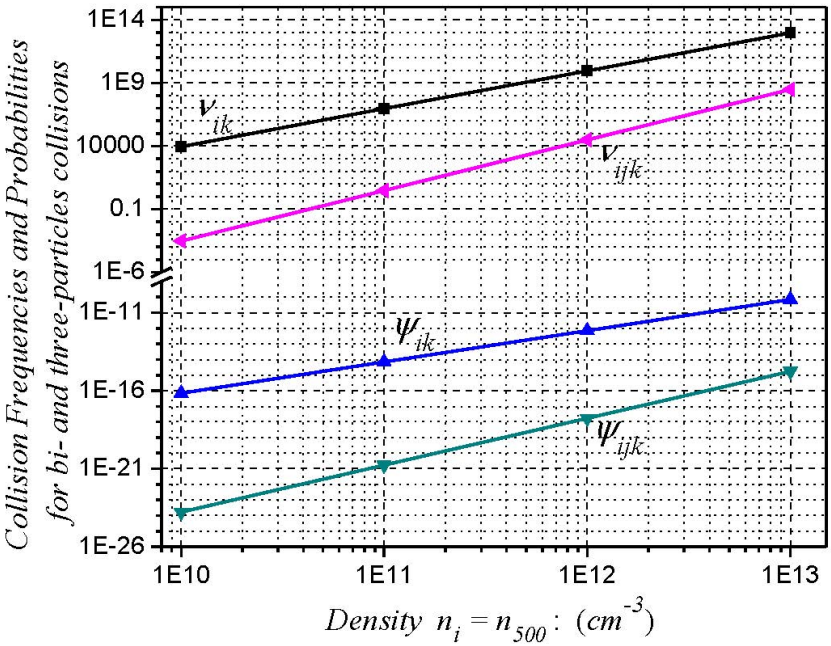

Figure 4. Collision frequency ν and probability ψ for bi- and three-particle collisions.

dominate over the bi-particle ones.

The collisions among atoms, molecules, and clusters are only the start of series of interactions leading to arise of larger nano sized particles. If the collided particles before collision possess a corresponding minimum amount of energy, called activation energy, the particles coalescence takes place. The part of coalesced particles C_{ik} per unit time per unit volume, at collisions among a_i and a_k particles, is determined by their frequency of collision ν_{ik}, by the probability for coalescence β_{ik}^{+} [43,44] and by the activation energy for their coalescence E_{ik} following the Arrhenius law:

$$C_{ik} = \nu_{ik}\beta_{ik}^{+}\exp\left(-\frac{E_{ik}}{RT}\right). \tag{15}$$

The growth of the nuclei occurs by joining of other atoms, molecules and clusters after collision with them. In this sense the knowledge of number of collisions per unit time per unit surface area of an arbitrary particle A_i ($A_i \in a_i$) obtained from the particles a_k is of great interest for the rate of nanoparticle formation and nuclei growth. The number of collisions per unit volume per unit time ν_{ik} among particles a_i and a_k is given by eq. 8. We assumed that the collisions ν_{ik} are equally distributed among the a_i-particles. By dividing ν_{ik} by

n_i, one obtains the number of collisions with the particles a_k registered by any particle $A_i \in a_i$ per unit time

$$\mathrm{N}_{A_i k} = \frac{\nu_{ik}}{n_i} = 3\pi^2 n_k \left(n_i \upsilon_i + n_k \upsilon_k\right) r_{ik}^5 (s^{-1}) \,. \tag{16}$$

Dividing the last equation by the surface area of the particle A_i one obtains the number of collisions per unit surface area per unit time

$$\eta_{A_i k} = \frac{\mathrm{N}_{A_i k}}{s_{ik}} = \frac{3\pi}{4} n_k \left(n_i \upsilon_i + n_k \upsilon_k\right) r_{ik}^3 (cm^{-2} s^{-1}) \,. \tag{17}$$

Quantities $\eta_{A_i k}$ and $\mathrm{N}_{A_i k}$ correspond with the nucleation rate in the crystal growth. The rate of homogeneous nucleation J has been defined as number of critical nuclei formed in unit volume per unit time. It affects the crystal growth rate and is a product of the critical nuclei's density n^* and the collisions N^* of these nuclei with all the other particles per unit time [56,57]

$$n^* = \mathrm{A} \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad \text{and} \quad J = \mathrm{N}^* \mathrm{A} \exp\left(-\frac{\Delta G^*}{k_B T}\right), \tag{18}$$

where ΔG^* is the energy, needed for formation of a critical nucleus. The number of collisions N_k^*, obtained from a critical nucleus by the particles a_k, may be determined by eq. 16 where the corresponding quantities n^*, n_k, υ^*, υ_k, $r_k^* = r^* + r_k$ (r^* is the critical nuclei radius) must be involved. The collisions with all the particles one obtains by summing over all values of $k \in (1, m)$, where m is the size of the largest particle a_m, consisting of $m-$atoms. The largest particle size a_m may correlate with the critical nuclei and at certain conditions may be identical with them $r^* \equiv r_m$. The radius r^* of the critical nucleus, obtained thermodynamically, is given by the expression $r^* = 2\sigma \upsilon_{\mathrm{mol}} / k_B T \ln S$ [56,57] where σ is the surface free energy of the nucleus, υ_{mol} is the volume of atom and/or molecule incorporated into the crystal and S is the super saturation ratio: $S = P/P_0$ in a gas phase growth process and $S = C/C_0$ – in a liquid phase one. P and C are the real values of the pressure and concentration respectively and P_0 and C_0 are their equilibrium values.

In consequence of collisions particles undergo either fusion or decay, or an energy exchange. The fusion of moving a_i and a_k particles may lead to their coalescence carrying out within a time interval $\Theta_{ik}^{(\mathrm{coal})}$ [52-54]. In case of very frequent collisions with period T_i and at $T_i < \Theta_{ik}^{(c)}$ it's no time for coalescence and both particles agglomerate. The time T_i may be determined by the number of collisions per unit time per unit particle in accordance with eq. 16. An arbitrary a_i particle obtains by the particles a_k $\mathrm{N}_i^{(k)}$ collisions per unit time. The period of these collisions is as follow (eq. 16):

$$T_i^{(k)} = \frac{1}{\mathrm{N}_i^{(k)}} = \frac{1}{3\pi^2 n_k \left(n_i \upsilon_i + n_k \upsilon_k\right) r_{ik}^5} \,. \tag{19}$$

In case of nearly equal sized particles $i = 500$ and $k = 600$ the period of collisions is $T_{500}^{(600)} \approx 10^6$ s at $n_{500} = 10^{10}$ cm^{-3}. With increasing particle density the period of collisions decreases very sharp – the rise of density by one order of magnitude causes a decrease of the period by two orders. At densities about 10^{19} cm^{-3} it is $T_{500}^{(600)} \approx 1$ ps.

In [52] using molecular dynamic simulation the coalescence of two spherical Si particles is considered. Particles are exposed to temperature 1500 K, where they are liquid and also to relative low temperature 1000 K – the particles are solid. In case of two liquid particles, consisting together of 10000 atoms, shared between both particles, at lower volume ratio $0,053$ the duration of the coalescence continues about 11 ps – this is the time interval from the moment of particle's approach by their spherical surfaces to the moment of formation of a spherical particle after coalescence. With increasing value of the volume ratio and at the same total number of atoms 10000 the coalescence continues longer time. For the solid particles the coalescence continues much longer because of the solid state diffusion.

One may expect that for two small particles, considered in our case, consisting together of 1100 atoms, the coalescence time will be about 1 ps at densities 10^{19} cm^{-3}. It means that in case of collision of these particles at densities lower than the threshold value of 10^{19} cm^{-3} they must coalescence but at larger densities they must agglomerate.

4 Conclusion

In the present work the frequency of collisions of moving particles has been considered. Obtained expression provides much smaller values for the frequency of bi-particle collisions, caused by the very low probability for simultaneous sojourn of both particles within the sphere of collisions. The case of three-particle collisions has been considered also and the corresponding relation concerning the collisions frequency is obtained. At densities above 10^{17} cm^{-3} the three-particle collisions predominate over the bi-particle ones. The number of collisions per unit time per unit surface area has been determined which correlates with the rate of nanoparticle formation and nuclei growth in case of homogeneous nucleation. The period of these collisions reveals the threshold value of density for taking place of particle coalescence or particle agglomeration.

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